Supplementary Material (ESI) for Chemical Communications

Supporting Information for:

Emulsion-assisted synthesis of monodisperse binary metal nanoparticles

Zhen Yin, Ding Ma* and Xinhe Bao*

Synthesis of the PdCu nanoparticles:

All synthesis was carried out under argon atmosphere. Typically, 1.5 mmol oleic acid (OA) and 1.5 mmol oleylamine (OAm) were mixed in the 50mL EG to form turbid solution under vigorous mechanical stir to which the two metal precursor solution of 0.5 mmol $Pd(CH_3COO)_2$ in acetone and 0.5 mmol $Cu(CH_3COO)_2 \cdot H_2O$ in distilled, deionized water (Nanopure, 18.2 MΩ·cm, purified with a Millipore Milli-Q water system) were then added. The mixture was stirred vigorously and first heated to 393 K for 30 min and the temperature was raised to reflux temperature (around 471 K) and kept at that temperature for 120 min with argon flow passing through the reaction system to take away water and acetone and other organic byproducts. After adding 50 mL hexane into the resulting mixture, it has broken into two layers with hexane at the top. It is interesting to see that the metal nanoparticles has been extracted into the hexane layer which is then concentrated in a rotary evaporator. After further centrifugation, washing with excess ethanol, the final product was dispersed in hexane and the solution was very stable without any aggregation after several months in the laboratory.

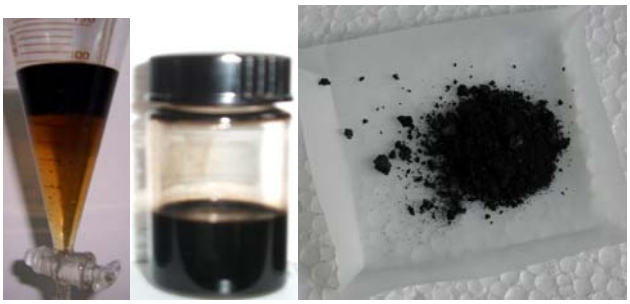


Figure S1. The synthesized PdCu nanoparticles: (Left) the distinguished layers of the mixture added the hexane after the reaction, the upward was the extraction solution of the nanoparticles, and (Middle) PdCu nanoparticles dispersion in hexane, and (Right) Dry powder of the PdCu nanoparticles after dried at 45℃ under vacuum.

Table S1. Experimental conditions for the preparation of bimetallic nanoparticles.

Bimetallic NPs	$Pd(OAc)_2$ (mmol)	$Au(OAc)_3$ (mmol)	Ag(OAc) (mmol)	$Cu(OAc)_2$ (mmol)	$Pt(OAc)_2$ (mmol)	OA,OAm (mmol)	EG (mL)	T (K)	Time (min)
PdAu	0.25	0.25				0.75	25	393	60
PdAg	0.5		0.5			0.75	50	393	60
PdCu	0.5			0.5		1.5	50	473	120
AuPt		0.25			0.25	0.75	25	393	90
AuAg		0.3	0.3			0.75	30	393	30

Characterization.

Electron microscope specimens were prepared by dispersing the suspension of nanoparticles in hexane and drop-casting it onto TEM copper-grids. Bimetallic PdCu sample were investigate onto TEM nickel-grids. TEM images were recorded on a FEI Tecnai G2 Spirit microscope equipped with a Gatan CCD camera and with an energy dispersive X-ray (EDX) system from EDAX Inc. at an accelerating voltage of 120 kV. The high resolution TEM (HR-TEM) images were recorded on a FEI Tecnai G2 microscope at an accelerating voltage of 300 kV equipped with an energy dispersive X-ray (EDX) system from EDAX Inc. with a point resolution of 0.20 nm. The composition of nanoparticles was analyzed by EDX and an inductively coupled plasma-atomic emission spectrometry (LEEMAN, PLASMA-SPEC- Ⅱ). Powder X-ray diffraction (PXRD) patterns were taken using a Rigaku D/max-2500 diffractometer with a Cu Kα X-ray source (λ=1.5405 Å) operated at 40 kV and 250 mA with a scan rate of 0.033° 2θ/s. The particle size distribution was obtained by analyzing at least 200 particles on the TEM images using the Image software from Gatan. The UV-vis spectra were acquired with a JASCO V-550 spectrophotometer from 200 to 900 nm. Nanoparticles solutions were in hexane.

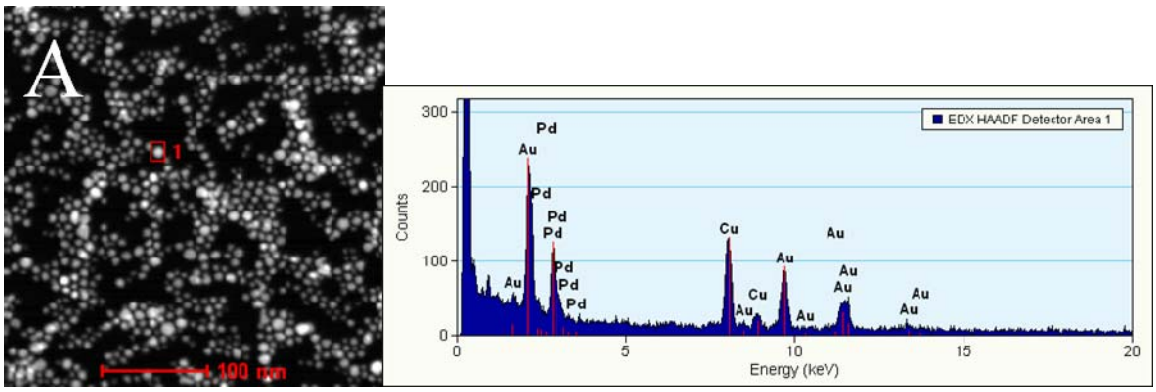


Figure S2. EDX of the single PdAu nanoparticle chosen randomly on the copper grid using the STEM-EDX.

Table S2. Elemental ratio for different individual PdAu bimetallic nanoparticle when the molar ratio of metal precursor is 1:1.

Nanoparticle	elemental ratio (Pd/Au) of each particle			
	1	2	3	Average
PdAu	28/72	37/62	26/74	31/69

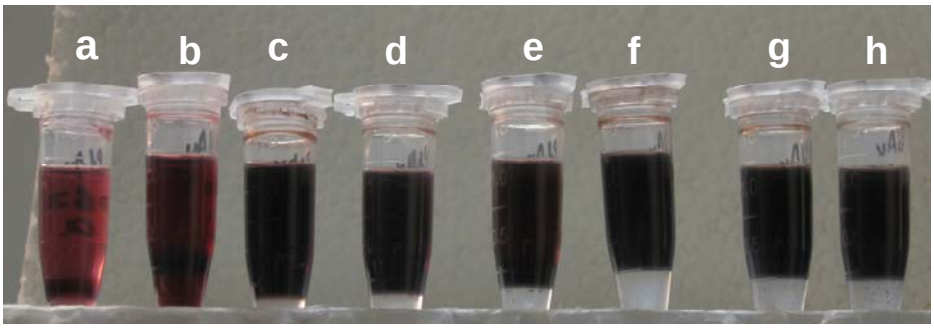


Figure S3. Color changes of the nanoparticles samples extracted from the reaction mixture with different temperatures and time intervals. The upper layer was the colloidal solution of nanoparticles in hexane. The bottom layer was the EG reaction solution. a) 373 K; b) 383 K; c) 393 K, 0 min; d) 393 K, 10 min, e) 393 K, 20 min; f) 393 K, 30 min; g) 393 K, 45 min; h) 393 K, 60 min.

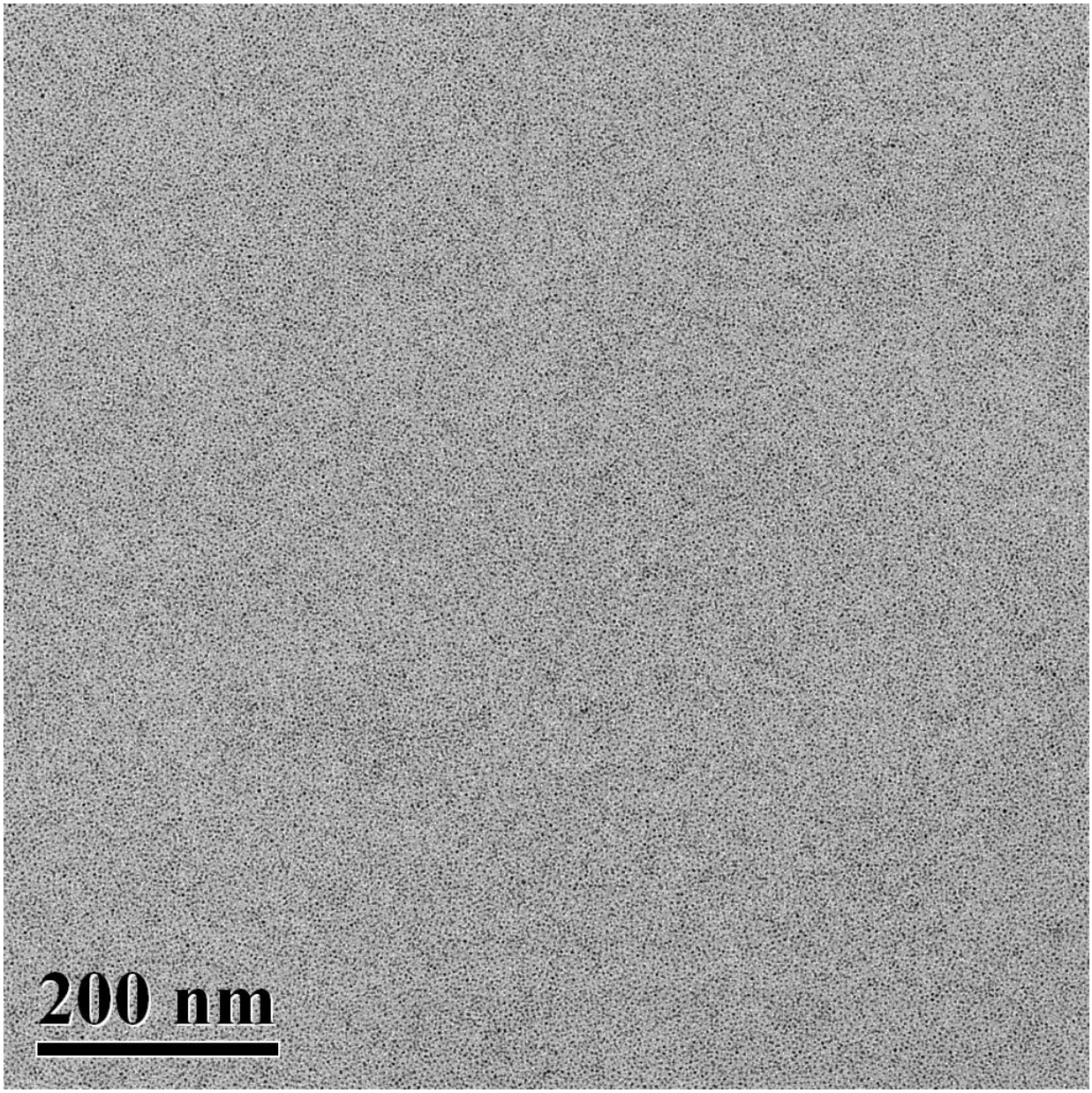
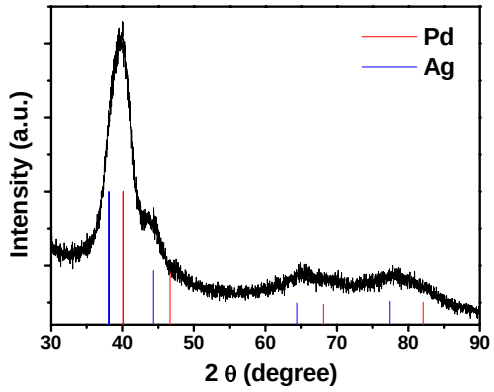
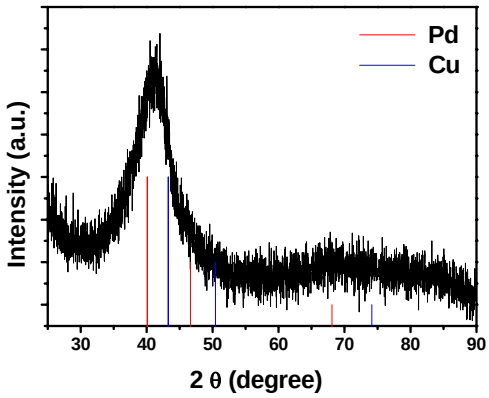
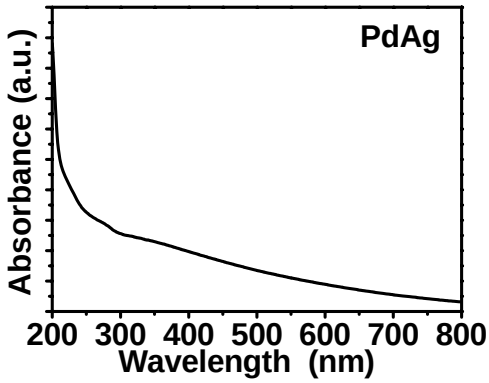
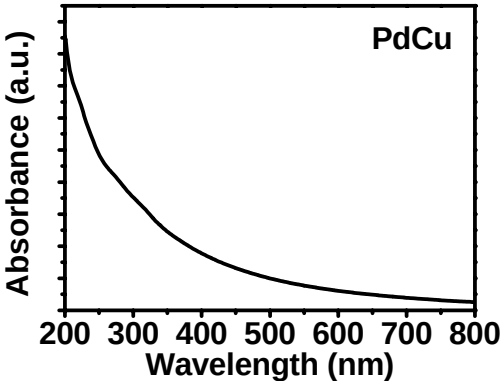


Figure S4. TEM image of large area of the monodisperse bimetallic PdCu nanoparticles with narrow size distribution at low magnification.









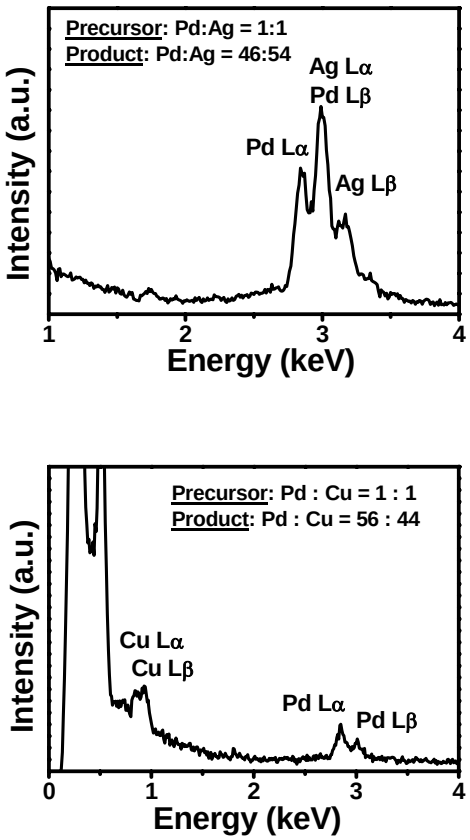


Figure S5. XRD pattern, UV-Vis spectra and EDX of the PdAg and PdCu bimetallic nanoparticles. Inset of EDX was shows that the structures contained bimetallic Pd-Ag and Pd-Cu nanoparticles with a molar ratio of 46:54 and 56:44, respectively, which was in good agreement with the molar ratios determined by ICP-AES in Table S3.

Table S3. Elemental ratio for different Pd-based bimetallic nanoparticles.

sample	Precursor molar ratios	Composition analyzed by EDX (molar ratio)	Composition analyzed by ICP (molar ratio)
PdAu	Pd:Au = 1:1	Pd:Au = 31:69	Pd:Au = 30:70
PdAg	Pd:Ag = 1:1	Pd:Ag = 46:54	Pd:Ag = 46:54
PdCu	Pd:Cu = 1:1	Pd:Cu = 56:44	Pd:Cu = 57:43

*EDX observation was conducted over an area containing several nanoparticles.

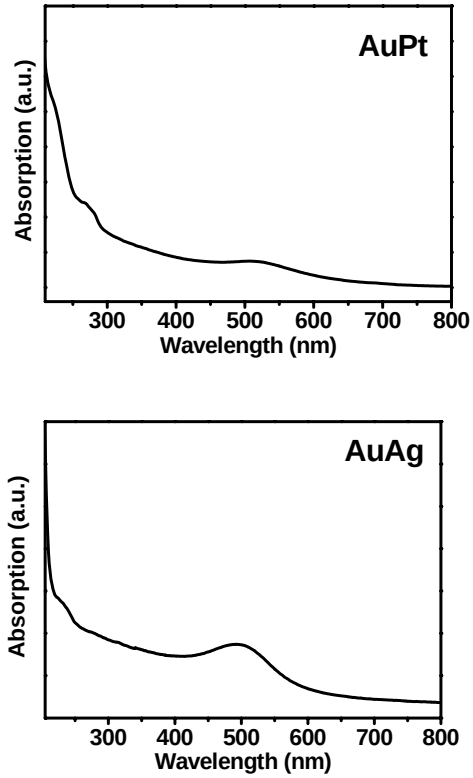


Figure S6. UV-Vis spectroscopy of binary metallic AuPt and AuAg nanoparticles.

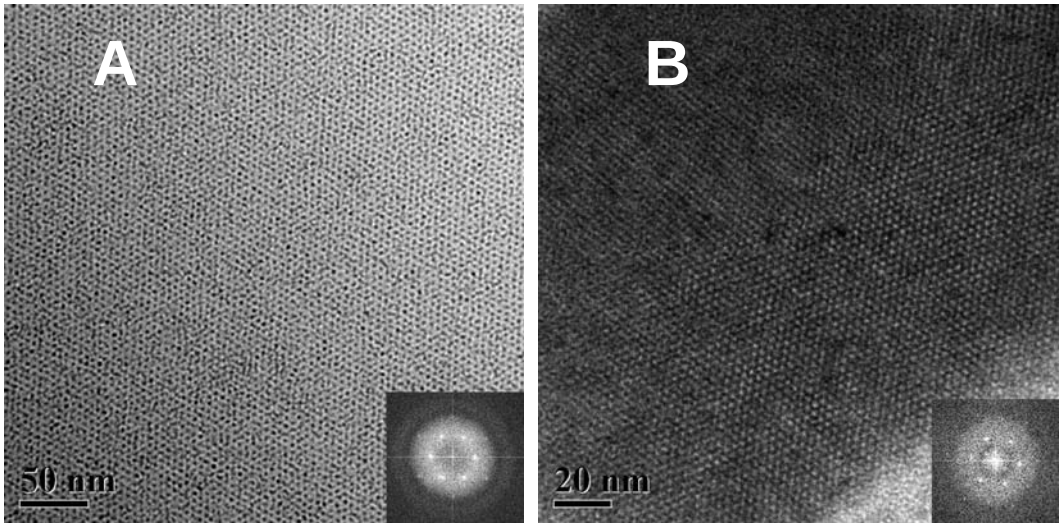


Figure S7. TEM images of 3-D superlattices from the bimetallic nanoparticles assembled on the copper grid: (A) PdAg and (B) AuAg. The inset is the FFT pattern of the supperlattice.